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(21) International Application Number: PCT/US99/04735 (22) International Filing Date: 3 March 1999 (03.03.99) (30) Priority Data: 09/034,443 4 March 1998 (04.03.98) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 09/034,443 (CON) Filed on 4 March 1998 (04.03.98) (71) Applicant (for all designated States except US): PHILLIPS PETROLEUM COMPANY [US/US]; 4th and Keeler, Bartlesville, OK 74004 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): SECORA, Steven, Joseph [US/US]; 5932 Martin Lane, Bartlesville, OK 74006 (US). EATON, Anthony, Patrick [US/US]; 301 Sally Lane, Dewey, OK 74029 (US). MCDANIEL, Max, Paul [US/US]; 1601 Melmart Drive, Bartlesville, OK 74006 (US). BENHAM, Elizabeth, Ann [US/US]; 431 Shannon, Bartlesville, OK 74006 (US).		(74) Agents: RICHARDS, John; Ladas & Parry, 26 West 61st Street, New York, NY 10023 (US) et al. (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: A PROCESS FOR POLYMERIZING AN OLEFIN (57) Abstract A process to control the polymer density in slurry ethylene polymerization processes comprising precontacting a catalyst system and cocatalyst for a time sufficient to reduce polymer density is provided. The catalyst system comprises chromium supported on a silica-titania support wherein the support comprises from about 2 to about 20 weight percent titanium, based on the weight of the support, and wherein the catalyst system has been activated in an oxygen-containing ambient and subsequently reduced in the presence of carbon monoxide. The cocatalyst is a trialkyl boron compound.		

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A PROCESS FOR POLYMERIZING AN OLEFIN

This invention relates to the copolymerization of mono-1-olefin monomers, such as ethylene, with at least one higher alpha-olefin comonomer.

It is well known that mono-1-olefins, such as ethylene, can be
5 polymerized with catalyst systems employing vanadium, chromium, or other metals on supports such as alumina, silica, aluminophosphate, titania, zirconia, magnesia and other refractory metals. Initially, such catalyst systems were used to form primarily homopolymers of ethylene. It soon developed, however, that many applications required polymers having more impact resistance than ethylene
10 homopolymers. Consequently, polymers were developed having short chain branching, like the more flexible free radical polymerized ethylene polymers, by adding comonomers such as propylene, butene, hexene and other higher alpha-olefins which were copolymerized with ethylene to provide resins tailored to specific end uses. These polymers, and processes to make such polymers, were
15 improved in order to more efficiently incorporate comonomers into the polymer to produce linear, low-density copolymers having high impact resistance, especially when made into films.

Based on commercial experience, it has been determined that, while numerous higher, alpha-olefin comonomers produce acceptable copolymer products,
20 ethylene/1-hexene copolymers are most desirable for best resultant polymer properties. Ethylene/1-butene copolymers also are commercially advantageous, but have properties that can be slightly inferior to ethylene/1-hexene copolymers.

In the past, it has been found that the addition of a cocatalyst, such as, for example, triethylboron (TEB), can produce a desirable result of increasing
25 the amount of branching resulting from comonomers produced in-situ. The addition of TEB, which is a relatively expensive cocatalyst, can also broaden the resultant polymer molecular weight distribution, and effect die swell, machine direction (MD) tear in film and other polymer properties. Unfortunately, while these secondary effects can be desirable in some applications, these effects can be undesirable in
30 other applications. For example, in addition to increased cost, high amounts of TEB in the reactor can be detrimental to MD tear resistance in film and decrease die swell in blow molding applications.

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The present invention provides an improved, more economical polymerization process.

The invention also provides a polymerization process that can produce copolymers of ethylene and one or more higher alpha-olefins having high impact resistance and toughness.

The invention further provides a process to control the quantity of comonomer(s) generated in-situ, and/or to decrease resultant polymer density without increasing the level of TEB cocatalyst added to the reactor, the invention providing a polymerization process in which by controlling in-situ comonomer production, copolymer density can be controlled.

The invention also deals with increasing comonomer incorporation into a resultant polymer and reducing the amount of comonomer recycled during a polymerization process.

In accordance with this invention, a process for polymerizing an olefin is provided which comprises contacting in a reaction zone under slurry polymerization reaction conditions, at a temperature within a range of about 90°C to 110°C:

- a) a diluent selected from the group consisting of paraffins, cycloparaffins, aromatic hydrocarbons, and mixtures thereof;
- b) ethylene monomer;
- c) at least one higher alpha-olefin comonomer having from about 3 to about 8 carbon atoms per molecule;
- d) a cocatalyst selected from the group consisting of alkyl boron compounds; and
- e) a catalyst system comprising chromium supported on a silica-titania support, wherein said support comprises from about 2 to about 20 weight percent titanium, based on the weight of the support, and wherein said catalyst system has been activated in an oxygen-containing ambient and subsequently reduced in the presence of carbon monoxide in an inert ambient; and wherein the catalyst system and cocatalyst are precontacted for a time sufficient to reduce polymer density.

In accordance with another embodiment of this invention, a process

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for polymerizing an olefin is provided which consists essentially of contacting in a reaction zone under slurry polymerization reaction conditions, at a temperature within a range of about 90°C to 110°C:

- a) a diluent selected from the group consisting of paraffins,
5 cycloparaffins, aromatic hydrocarbons, and mixtures thereof;
- b) ethylene monomer;
- c) at least one higher alpha-olefin comonomer having from about 3 to about 8 carbon atoms per molecule;
- d) a cocatalyst selected from the group consisting of alkyl boron
10 compounds; and
- e) a catalyst system comprising chromium supported on a silica-titania support, wherein said support comprises from about 2 to about 20 weight percent titanium, based on the weight of the support, and wherein said catalyst system has been activated in an oxygen-containing ambient and
15 subsequently reduced in the presence of carbon monoxide in an inert ambient; and wherein the catalyst system and cocatalyst are precontacted for a time sufficient to reduce polymer density.

In accordance with still another embodiment of this invention the catalyst system and alkyl boron cocatalyst are precontacted for a time within a range
20 of about 1 minute to about 60 minutes prior to contacting ethylene monomer.

As used in this disclosure, the term "polymer" and "copolymer" are used interchangeably, and both terms include the product of polymerizing ethylene and a higher alpha-olefin comonomer including, but not limited to, 1-butene, 1-pentene, 1-hexene, 1-octene, and/or 4-methyl-1-pentene.

25 Catalyst Systems

Catalyst systems used in this invention must be supported chromium catalyst systems. The chromium catalyst systems of this invention comprise chromium supported on a silica-titania support. The catalyst support must be a silica-titania support. As used in this disclosure, the term "support" refers to a
30 carrier for another catalytic component. However, by no means is a support necessarily an inert material; it is possible that a support can contribute to catalytic activity and selectivity. Further, as used in this application, reference to silica

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means a silica-containing material generally composed of 80 to 100 weight percent silica, the remainder, if any, being selected from alumina, boria, magnesia, thoria, zirconia, or mixtures thereof. For instance, the silica-containing material can consist essentially of silica and no more than 0.2 weight percent of alumina or other metal oxide. Other ingredients which do not adversely affect the catalyst system, or which are present to produce some unrelated result, can also be present. Preferably, the support contains from about 2 to about 20 weight percent titanium (Ti), based on the total weight of the dry support. Most preferably, the support contains 3 to 6 weight percent titanium, in order to produce a polymer with the most desirable physical properties. The most preferred support is a cogelled silica/titania support in order to produce a polymer with the desired physical characteristics. Silica-titania supports are well known in the art and can be produced as disclosed in Dietz, U.S. Pat. No. 3,887,494.

The catalyst component of the catalyst system must be a chromium compound. The chromium component can be combined with the silica-titania support component in any manner known in the art, such as for example, forming a coprecipitated tergel of the silica, titanium, and chromium components. Alternatively, an aqueous solution of a water-soluble chromium component can be added to a hydrogel of the silica-titanium component. Suitable water-soluble chromium compounds include, but are not limited to, chromium nitrate, chromium acetate, and chromium trioxide. Alternatively, a solution of a hydrocarbon-soluble chromium component such as tertiary butyl chromate, a diarene chromium compound, biscyclopentadienyl chromium(II) or chromium acetylacetonate can be used to impregnate the silica-titania xerogel which results from removal of water from the cogel. The chromium component is used in an amount sufficient to give from about 0.05 to about 5, preferably 0.5 to 2, weight percent chromium, based on the total weight of the chromium and support after activation.

The resulting chromium component on the silica-titania support is then subjected to activation in an oxygen-containing ambient in any manner conventionally used in the art. Because of economy and ease of use, the preferred oxygen-containing ambient is air, preferably dry air. Activation can be carried out at an elevated temperature for about one-half to about 50 hours, preferably about 2

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to about 10 hours at a temperature within the range of about 300° to about 1000°C, preferably about 300° to about 800°C, and most preferably within a range of 600° to 700°C. Under these activation, or calcination, procedure conditions, at least a substantial portion of any chromium in a lower valent state is converted to the hexavalent state.

The resulting calcined, supported catalyst component is cooled and then must be subjected to at least a partial reduction of the hexavalent chromium to a lower valence state prior to combining with a cocatalyst. The reducing agent must be carbon monoxide in order to effectively incorporate a comonomer into the copolymer. If a reducing agent other than carbon monoxide is used catalyst system activity can be decreased and/or higher amounts of comonomer can be needed in the reaction zone to achieve similar amounts of comonomer incorporation into the resultant copolymer. Generally, the calcined catalyst is directly subjected to the reducing agent, although intervening steps may be employed, if desired.

The carbon monoxide reduction process can be employed at temperatures between about 300° to about 500°C, although it is preferably employed at temperatures in a range of 350° to 450°C for best chromium reduction. The partial pressure of the reducing gas in the reduction operation can be varied from sub-atmospheric pressures to relatively high pressure, but the simplest reducing operation is to utilize about 5 to about 25 volume percent carbon monoxide, diluted with nitrogen, at about atmospheric pressure.

The reduction time can vary from a few minutes to several hours or more. The extent of the reduction can be followed by visual inspection of catalyst color. The color of the initial activated catalyst is generally orange, indicating the presence of hexavalent chromium. The color of the reduced catalyst system employed in the invention is blue, indicating that all or substantially all of the initial hexavalent chromium has been reduced to lower oxidation states, generally the divalent state.

The course of the reduction of the air-activated orange catalyst with carbon monoxide can be determined exactly by pulse titration. A known amount of carbon monoxide is added per pulse and the amount of evolved carbon dioxide is measured. When reduction is complete only carbon monoxide will be present and

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the catalyst system is blue in color. The reduced blue catalyst system can be titrated with pulses of oxygen to convert the catalyst system to the original orange color. When oxidation is complete, oxygen will be evident in the off gas.

After reduction, the reduced, supported catalyst system is cooled to
5 about room temperature, e.g, about 25°C, in an inert atmosphere such as argon or nitrogen to flush out carbon monoxide. After this flushing treatment, the catalyst system is kept away from contact with either reducing or oxidizing agents, i.e., carbon monoxide and oxygen.

Catalyst systems of this invention must be used in conjunction with
10 an alkyl boron cocatalyst. Exemplary alkylboron compounds include, but are not limited to, trialkyl boron compounds, particularly tri-n-butylborane, tripropylborane, and triethylborane (TEB). Other suitable boron compounds include trihydrocarbyl boron compounds broadly; triaryl boron compounds, such as, for example, triphenylborane; and boron alkoxides, such as, for example, $B(C_2H_5)_2(OC_2H_5)$.
15 Halogenated alkyl boron compounds, such as, for example, $B(C_2H_5)Cl_2$, can be used as cocatalysts but are not as preferred because they can inhibit catalyst system activity and comonomer in-situ production and incorporation.

Preferably, the cocatalyst is a trialkyl boron compound, wherein the alkyl group has from about 1 to about 10 carbon atoms and preferably from 2 to 4
20 carbon atoms per alkyl group. Trialkyl boron compounds are preferred cocatalysts because these compounds are effective agents to improve polymer properties, such as, for example, to reduce melt flow and to retard polymer swelling during polymerization. By far, the most preferred alkylboron cocatalyst is triethyl borane, for the reasons given above.

25 The cocatalyst can be used in an amount within a range of about 0.1 to about 20 parts per million (ppm), or milligrams per kilograms (mg/kg), based on the mass of diluent in the reactor. Preferably, cocatalyst is used in an amount within a range of 0.5 to 12 mg/kg, and most preferably within a range of 0.5 to 6 mg/kg, for cost effectiveness and best resultant polymer properties.

30 Reactants

Polymers produced according to this invention must be copolymers. This inventive process is of particular applicability in producing copolymers of

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ethylene and higher alpha-olefins. Ethylene monomer must be polymerized with at least one higher alpha-olefin comonomer having from about 3 to about 10 carbon atoms per molecule. Preferably, the higher alpha-olefin comonomer is selected from the group consisting of 1-butene, 1-pentene, 1-hexene, 1-octene,
5 4-methyl-1-pentene, and mixture thereof. Ethylene monomer is the necessary monomer due to the advantageous physical properties of the resultant copolymer. Most preferably, the comonomer is 1-butene and/or 1-hexene, to achieve maximum polymer toughness.

The contents of a polymerization reactor can be determined by a
10 variety of different methods. One method is to measure the amount of each reactant actually fed to the reactor. A second method is to sample the flash gas at a reactor outlet and then analyze the flash gas sample for reactant quantities. Due to reactor operating conditions, it is very unsafe and nearly impossible to sample the actual contents of the reactor. Usually, during a commercial polymerization process, a
15 flash gas sample is used to determine reactor comonomer and monomer concentrations.

The total comonomer to monomer weight ratio added to the polymerization reactor, or reaction zone, during normal polymerization conditions can vary greatly. As used in this disclosure, "normal" polymerization conditions are
20 those which are used most often for polymerization. The amount of comonomer content in the reactor feed includes comonomer which is added fresh to the reactor and comonomer which is recycled back into the reactor after recovery of the polymer. Usually the monomer weight feed ratio is within a range of about 0.03 to about 0.4; i.e., a range of about 3 parts by weight of comonomer per 100 parts by
25 weight of ethylene to about 40 parts by weight comonomer per 100 parts by weight ethylene.

While not wishing to be bound by theory, it is believed that additional comonomers, as disclosed earlier, can be generated in-situ in the polymerization reactor, or the reaction zone, as disclosed in U.S. Pat. No. 4,820,785
30 (McDaniel et al, 1988). Since more than one comonomer can be generated in-situ, the resultant copolymer product can have more than one comonomer incorporated into the copolymer.

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Polymerization

Polymerization of the monomer and comonomer must be carried out under slurry, also known as loop/slurry or particle form, polymerization conditions wherein the temperature is kept below the temperature at which polymer swells significantly. The slurry polymerization process is relatively simple, compared to other polymerization processes and the polymer product can be recovered much more easily. Such polymerization techniques are well-known in the art and are disclosed, for instance, in Norwood, U.S. Pat. No. 3,248,179. The slurry process is generally carried out in an inert diluent (medium), such as, for example, a paraffin, cycloparaffin, and/or aromatic hydrocarbon. Exemplary diluents include, but are not limited to propane, n-butane, isobutane, n-pentane, 2-methylbutane (isopentane), and mixtures thereof. Isobutane is the most preferred diluent due to low cost and ease of use.

The temperature of the polymerization reactor, or reaction zone, when using isobutane as the reactor diluent, according to this invention, is critical and must be maintained within a range of about 90°C (194°F) to about 110°C (230°F), and more preferably within a range of about 93°C (199°F) to about 107°C (225°F). Most preferably, the reaction zone temperature is within a range of 95°C (203°F) to 105°C (221°F). Although higher reactor temperatures can be used, operating outside of the specified temperature ranges can cause the copolymer to swell and the reactor to foul irreversibly.

Pressures in a slurry process can vary from about 110 to about 700 psia (0.76-4.8 MPa) or higher. The catalyst system is kept in suspension and is contacted with the monomer and comonomer(s) at sufficient pressure to maintain the medium and at least a portion of the monomer and comonomer(s) in the liquid phase. The medium and temperature are thus selected such that the copolymer is produced as solid particles and is recovered in that form. Catalyst system concentrations in the reactor can be such that the catalyst system content ranges from 0.001 to about 1 weight percent based on the weight of the reactor contents.

Two preferred polymerization methods for the slurry process are those employing a loop reactor of the type disclosed in Norwood and those utilizing a plurality of stirred reactors either in series, parallel or combinations thereof

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wherein the reaction conditions can be the same or different in the different reactors. For instance, in a series of reactors, a chromium catalyst system which has not been subjected to the reduction step can be utilized either before or after the reactor utilizing the catalyst system of this invention. In another specific instance, a
5 conventional chromium oxide catalyst system can be utilized in a reactor in parallel with a reactor utilizing the catalyst system of this invention and the resulting polymerization diluents can be combined prior to recovering copolymer.

The molecular weight of the copolymer can be controlled by various means known in the art such as adjusting the temperature of the reaction zone
10 (higher temperature giving lower molecular weight), introducing hydrogen to lower the molecular weight or varying the catalyst system compounds.

In accordance with this invention, the catalyst system and trialkyl boron cocatalyst must be precontacted prior to contact with monomer and comonomer. It has been discovered that increasing precontact times can reduce
15 polymer density. Precontacting of the catalyst system and cocatalyst is essential to control resultant polymer density. Hereinafter, the precontacted catalyst system and trialkyl boron cocatalyst is referred to as the "combined catalyst system."

Precontact times of at least one (1) minute are needed to reduce polymer density. Preferably, precontact times are within a range of about two (2) minutes to about 30
20 minutes. Most preferably, precontact times are within a range of three (3) minutes to 20 minutes, for best density control. Longer precontact times do not significantly increase density reduction and too short of a precontact time can result in no effect on polymer density.

Precontacting of the catalyst system and cocatalyst can occur in
25 accordance with any method known in the art and must be done in the absence of oxidizing agents, such as, for example, air or oxygen. Preferably, the catalyst system and cocatalyst are in liquid form during precontacting. If necessary, precontacting can occur in the presence of inert ambients, such as, for example, nitrogen and/or argon. Nitrogen is most preferred due to availability and ease of
30 use.

After precontacting the catalyst system and cocatalyst, i.e., the combined catalyst system, and monomer and comonomer(s) can be added to the

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reaction zone in any order, according to any method known in the art. For example, the combined catalyst system, monomer, and comonomer can be added simultaneously to the reaction zone. If desired, the catalyst system and cocatalyst can be precontacted and stored under an inert ambient prior to contacting the monomer and/or comonomer. If the catalyst and cocatalyst are precontacted, as disclosed by McDaniel et al in U.S. Pat. No. 4,735,931, some comonomer can be generated in-situ; therefore, the amount of comonomer that is affirmatively added to the reaction zone can be reduced, but still remain within the ranges disclosed above.

During normal polymerization conditions, when making a polymer within a density range of about 0.918 to about 0.925 g/cc, the comonomer to ethylene monomer weight ratio, as stated earlier, generally is within a range of about 0.03 to about 0.4 and generally within a range of about 0.03 to about 0.15. However, this feed weight ratio can vary depending on the type of polymer desired. Expressed in different terms, the comonomer to ethylene monomer feed ratio points generally are within a range of about 3 to about 40 and generally within a range of about 2 to about 15.

Product

Polymers produced in accordance with this invention must be a copolymer of ethylene and at least one higher alpha-olefin. The comonomer, or higher alpha-olefin, whether affirmatively added or generated in-situ in the polymerization reactor, is very efficiently incorporated into the copolymer. The copolymer product contains from about 7 to about 15 weight percent, preferably from about 8 to about 12 weight percent comonomer, based on the total weight of the copolymer product. Most preferably, the comonomer is present in the copolymer with the range of 8 to 10 weight percent for the best copolymer properties and reactor run conditions.

Copolymers produced according to this invention generally are impact resistant, tough, linear, low-density polyethylene copolymers, having a broad molecular weight distribution. Usually, the melt index (MI) for polymers produced in accordance with this invention, before pelletizing, are within a range of about 0.05 to about 0.35 g/10 min., preferably within a range of about 0.05 to about 0.3 g/10 min. Most preferably, the inventive polymers have a MI within a range of 0.2

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to 0.3, for best processability and best melt strength, i.e., toughness. Usually, the high load melt index (HLMI) for polymers produced in accordance with this invention are within a range of about 15 to about 40 g/10 min., and preferably within a range of about 20 to about 30 g/10 min. Most preferably, the polymers
5 have a HLMI within a range of 23 to 29, for best processability and melt strength, i.e., toughness. Generally, as HLMI decreases, processing difficulty increases; however, as HLMI decreases, polymer melt strength also increases. Therefore, polymers of this invention usually have a HLMI/MI ratio, before pelleting, within a range of about 60 to about 150, preferably within a range of about 70 to about 120.
10 Most preferably, the HLMI/MI ratio is within a range of 80 to 100, for the reasons given above.

The density of the copolymer products produced in accordance with this invention are less than or equal to 0.930 g/cc preferably from about 0.915 to about 0.925 g/cc. Most preferably, the copolymer density is within the range of
15 0.918 to 0.922 g/cc.

Other aspects and embodiments of this invention can be shown by the following examples.

Examples

Ethylene and higher alpha-olefin copolymers were prepared under
20 continuous particle form process conditions, as described in the following Examples.

Polymer product was collected from each run and tested according to the following procedures:

Density (g/ml): ASTM D 1505-68 and ASTM D 1928, Condition C. Determined on a compression molded sample, cooled at about 15°C per minute, and
25 conditioned at room temperature for about 40 hours.

High Load Melt Index (HLMI)(g/10 min): ASTM D1238, condition E. Determined at 190°C with a 21,600 gram weight.

Heterogeneity Index (HI): M_w/M_n

Example I

30 The polymerization process used in this Example comprised contacting the catalyst system with ethylene and a comonomer in a 2.3 liter, jacketed, bench scale autoclave reactor. Isobutane was the diluent; comonomer and

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hydrogen 0.2 mole % in the flash gas) were added to the reactor. The reactor was operated for a time of 60-75 minutes. Reactor temperature was 203°F (95°C) and total reactor pressure (isobutane plus ethylene) was 3.8 MPa (550 psig). The catalyst system used is a commercially available catalyst system, purchased from W.R. Grace and Company, the Davison business unit, designated as 964 Magnapore® Catalyst system was activated at 1200°F (649°C) and subsequently reduced with carbon dioxide. Results are shown below in Table 1.

TABLE 1

Run	Precontact Time (Minutes)	Polymer Density (g/cc)
101	0	0.957
102	0.5	0.948
103	4	0.948
104	10	0.946

The data in Table 1 show that at a constant TEB concentration, comonomer production varied as indicated by resultant copolymer density. As precontact time increases, comonomer production increases and copolymer density decreases.

Example II

The polymerization process used in this Example comprised contacting catalyst with monomers, employing a liquid full loop reactor, having a volume of 23 gallons (87 liters), isobutane as the diluent, and occasionally some hydrogen, as shown in the Examples. The reactor was operated to have a residence time of 1.25 hrs. The reactor temperature was varied over the range of 94°C to 106°C, unless shown differently, and the pressure was 3.75 MPa (530 psi). At steady state conditions, the isobutane feed rate was 54 lbs/hr, the ethylene feed rate was about 24 lbs/hr, and the 1-hexene feed rate was varied to control the density of the product polymer. Polymer was removed from the reactor at the rate of 22 lbs/hr.

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TABLE 2

RUN	TEB Feed Rate ^(a) (lbs/hr)	TEB Conc. ^(a) (ppm)	Precontactor Residence Time ^(a) (mins)	Density (g/cc)	HLMI (fluff) (g/10mins)	HLMI (pellet) (g/10mins)
5						
201	0.325	1.5	7.93	0.939	20.60	18.04
202	0.316	1.5	7.27	0.940	17.65	16.02
10						
203	0.309	1.4	6.47	0.934	20.75	18.00
204	0.325	1.6	6.30	0.940	20.29	16.62
205	0.347	1.6	7.42	0.940	19.76	16.73
15						
206	0.349	1.6	8.79	0.940	18.52	15.95
207	0.344	1.6	15.71	0.937	19.57	16.49
20						
208	0.327	1.5	6.93	0.940	18.20	15.81
209	0.314	1.5	4.48	0.941	16.49	14.55
210	0.311	1.5	4.23	0.941	18.16	15.98

25 ^(a) Values given are a 6-hour average.

The data in Table 2 show, again, that at a constant TEB concentration, comonomer production varied as indicated by resultant copolymer density. As precontact time increases, comonomer production increases and copolymer density decreases. The trend of precontact time versus density is a linear relationship, with a coefficient of determination (line slope) of 0.91. Thus, a definitive relationship between precontacting time and comonomer production is demonstrated.

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While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

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CLAIMS

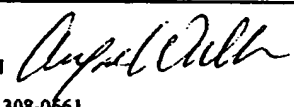
1. A process for polymerizing an olefin which comprises contacting in a reaction zone under slurry polymerization reaction conditions, at a temperature within a range of about 90°C to 110°C:
 - 5 a) a diluent which is a paraffin, a cycloparaffin, an aromatic hydrocarbon, or a mixture of any two or more of said diluents;
 - b) ethylene monomer;
 - c) at least one higher alpha-olefin comonomer having from about 3 to about 8 carbon atoms per molecule;
 - 10 d) a cocatalyst which is an alkyl boron compound; and
 - e) a catalyst system comprising chromium supported on a silica-titania support, wherein said support comprises from about 2 to about 20 weight percent titanium, based on the weight of the support, and wherein said catalyst system has been activated in an oxygen-containing ambient and subsequently
 - 15 reduced in the presence of carbon monoxide in an inert ambient; andwherein the catalyst system and the cocatalyst are precontacted for a time sufficient to reduce polymer density.
2. A process according to claim 1, which consists essentially of the enumerated steps.
- 20 3. A process according to claim 1, wherein said temperature in the reaction zone is within a range of from about 60°C to about 88°C.
4. A process according to any one of the preceding claims, wherein said cocatalyst is a trialkyl boron compound which is tri-n-butylborane, tripropylborane, or triethylborane.
- 25 5. A process according to claim 4, wherein said trialkyl boron compound is triethylborane and is present in the reaction zone in a range of from about 1 to about 20 ppm, based on the mass of the diluent.
6. A process according to any one of claims 1-5, wherein said higher alpha-olefin comonomer is 1-butene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-
- 30 pentene, or a mixture of any two or more of said comonomers.
7. A process according to claim 6, wherein said comonomer is 1-hexene or 1-butene.

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8. A process according to any one of claims 1-5, wherein said catalyst system has been activated in air at a temperature in a range of from about 300° to about 1,000°C and wherein said carbon monoxide reduction is carried out at a temperature in a range of from about 300° to 500°C.
- 5 9. A process according to any one of claims 1-5, wherein said silica-titania support is formed by coprecipitation.
10. A process according to any one of claims 1-5, wherein said catalyst system and said cocatalyst are precontacted for a time of greater than one (1) minute.
- 10 11. A process according to claim 10, wherein said catalyst system and said cocatalyst are precontacted for a time within a range of about two (2) minutes to about thirty (30) minutes.
12. A process for polymerizing an olefin substantially as herein described.
- 15 13. A process for polymerizing an olefin substantially as herein described with reference to any of the Examples.
14. A polymer when produced by a process according to claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/04735

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) :C08F 4/24 US CL :526/106, 348, 351, 352 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 526/106, 348, 351, 352 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,735,931 A (MCDANIEL et al) 05 April 1988, see columns 1-4 and examples 1-3 and 7.	1-14
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* "A" "B" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family
Date of the actual completion of the international search 09 JUNE 1999		Date of mailing of the international search report 28 JUN 1999
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